

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER

218450US6PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

10/030144

INTERNATIONAL APPLICATION NO.

PCT/EP00/06970

INTERNATIONAL FILING DATE

20 JULY 2000

PRIORITY DATE CLAIMED

27 JULY 1999

TITLE OF INVENTION

PROCESS FOR INTRODUCING AT LEAST ONE CHEMICAL COMPOUND INTO AN EXTRUDER,
INTRODUCTION DEVICE, EXTRUDER EQUIPPED WITH SUCH A DEVICE AND PROCESSES USING SUCH

APPLICANT(S) FOR DO/EO/US

Dino MANFREDI, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☒ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Notice of Priority / PTO-1449

Drawing (1 sheet)

Amended Sheets (pages 12, 13 and 14)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

10/030144

INTERNATIONAL APPLICATION NO.

PCT/EP00/06970

ATTORNEY'S DOCKET NUMBER

218450US6PCT

24. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1040.00
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).

☐ 20☒ 30

\$130.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	- 20 =	0	x \$18.00	\$0.00
Independent claims	- 3 =	0	x \$84.00	\$0.00
Multiple Dependent Claims (check if applicable)			<input type="checkbox"/>	\$0.00

TOTAL OF ABOVE CALCULATIONS =

\$1,020.00

☒ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.

\$0.00

SUBTOTAL =

\$1,020.00

Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (i)).

☐ 20☐ 30

+

\$0.00

TOTAL NATIONAL FEE =

\$1,020.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).

☐

\$0.00

TOTAL FEES ENCLOSED =

\$1,020.00

Amount to be:	S
refunded	
charged	S

- ☒ A check in the amount of \$1,020.00 to cover the above fees is enclosed.
- ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



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SIGNATURE

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NAME

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REGISTRATION NUMBER

DATE

Jan 28 2002

#4

218450US-9458-9459-6-PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :
 DINO MANFREDI ET AL. : ATTN: APPLICATION DIVISION
 SERIAL NO: 10/030,144 :
 FILED: JANUARY 28, 2002 : EXAMINER:
 FOR: PROCESS FOR INTRODUCING :
 AT LEAST ONE CHEMICAL COMPOUND
 INTO AN EXTRUDER, INTRODUCTION
 DEVICE, EXTRUDER EQUIPPED WITH
 SUCH A DEVICE AND PROCESSES USING
 SUCH AN EXTRUDER

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
 WASHINGTON, D.C. 20231

SIR:

Prior to a first examination on the merits, please amend the above-identified
 application as follows:

IN THE CLAIMS

Please cancel Claims 1-14 without prejudice.

Please add new Claims 15-28 as follows:

15. (New) Process for introducing at least one chemical compound into an extruder,
 comprising:

introducing a material to be extruded into the extruder;

introducing at least one mixture of at least one chemical compound and of carbon
 dioxide into the extruder by at least one introduction device comprising at least two pumps, a
 mixing chamber, and an injector placed to be perpendicular to a barrel of the extruder; and

extruding the material together with the at least one mixture.

16. (New) Process according to Claim 15, wherein the at least one mixture of at least one chemical compound and of carbon dioxide is introduced into a zone of the extruder where the material to be extruded is in a fluidized state.

17. (New) Process according to Claim 15, wherein the at least one chemical compound is in a fluidized state.

18. (New) Device for introducing at least one chemical compound into an extruder, comprising at least two pumps, a mixing chamber, and an injector.

19. (New) Device according to Claim 18, wherein the at least two pumps comprise:
a first pump for feeding at least one chemical compound into the mixing chamber;
and
a second pump for feeding carbon dioxide into the mixing chamber.

20. (New) Device according to Claim 19, wherein the carbon dioxide is cooled before it enters the second pump.

21. (New) Device according to Claim 18, wherein the mixing chamber includes a stirring system.

22. (New) Device according to Claim 18, wherein a pressure in the injector is measured by a pressure sensor.

23. (New) Extruder, comprising a feed zone, a compression zone, and a discharge zone, equipped with at least one introduction device according to Claim 18.

24. (New) Extruder according to Claim 23, further comprising an extrusion screw and a barrel, in which the injector of each introduction device is placed to be perpendicular to the barrel of the extruder and emerges tangentially with respect to screw flights of the extrusion screw.

25. (New) Extruder according to Claim 23, wherein the injector of each introduction device is placed to be perpendicular to a zone in which the material to be extruded is in a fluidized state.

26. (New) Process for extruding a polymeric material by an extruder according to Claim 23, comprising:

introducing a polymeric material into the extruder;

in each introduction device present:

introducing at least one chemical compound into the mixing chamber;

introducing precooled carbon dioxide into the mixing chamber; and

mixing the at least one chemical compound and the carbon dioxide in the mixing chamber;

introducing the mixture thus obtained into the extruder; and

extruding polymeric material together with the mixture.

27. (New) Process for modifying a polymeric material by an extruder according to Claim 23, comprising:

introducing a polymeric material into the extruder;

in each introduction device present:

introducing at least one chemical compound into the mixing chamber;

introducing precooled carbon dioxide into the mixing chamber; and

moving the at least one chemical compound and the carbon dioxide in the mixing chamber;

introducing the mixture thus obtained into the extruder; and

extruding polymeric material together with the mixture under conditions allowing a reaction between at least one of the chemical compounds and the polymeric material.

28. (New) Process for synthesizing a polymeric material by means of an extruder according to Claim 23, comprising:

introducing a material to be polymerized into the extruder;

in each introduction device present:

introducing at least one chemical compound into the mixing chamber;

introducing precooled carbon dioxide into the mixing chamber; and

mixing the at least one chemical compound and the carbon dioxide in the mixing chamber;

introducing the mixture thus obtained into the extruder; and

extruding the material to be polymerized together with the mixture under conditions allowing a reaction between at least one of the chemical compounds and the material to be polymerized, and the polymeric material thus formed is extruded.

IN THE ABSTRACT

Please delete the original Abstract on page 15 in its entirety and insert therefor:

ABSTRACT

A process for introducing at least one chemical compound into an extruder, an introduction device, an extruder equipped with such an introduction device, and a process for using such an extruder. The process for introducing the at least one chemical compound into the extruder introduces a material to be extruded into the extruder, introduces at least one mixture of at least one chemical compound and of carbon dioxide into the extruder, and extrudes the material together with the at least one mixture. A device introduces the at least one chemical compound into the extruder, and the extruder is equipped with such an introduction device. Such processes and devices are particularly suited for synthesizing a polymeric material, as an example.

REMARKS

Favorable consideration of this application, as presently amended, is respectfully requested.

The present preliminary amendment is submitted to place the above-identified application in more proper format under United States format.

By the present preliminary amendment Claims 1-14 are cancelled and new Claims 15-28 are presented for examination. New Claims 15-28 are deemed to be self-evident from the original disclosure, including the original claims, and thus are not deemed to raise any issues of new matter. New Claims 15-28 have been written to be in more proper format under United States practice and to more clearly recite the claimed features. New Claims 15-28 are not believed to be narrowed in scope in any aspect with respect to the original claims.

A new Abstract believed to be in more proper format under United States practice is also submitted herein.

The present application is believed to be in condition for a full and thorough examination on the merits. An early and favorable consideration of the present application is hereby respectfully requested.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.



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Marked-Up Copy

Serial No: 10/030,144

Amendment Filed on:

4-30-02

IN THE CLAIMS

Claims 1-14 (Cancelled).

Claims 15-28 (New).

IN THE ABSTRACT

(New).

Process for introducing at least one chemical compound into an extruder,
introduction device, extruder equipped with such a device and processes using
such an extruder

5 The invention relates to a process for introducing at least one chemical compound into an extruder, to a device for introducing at least one chemical compound into an extruder, to an extruder equipped with at least one introduction device as well as to a process for extruding, a process for modifying and a process for synthesizing a polymeric material by means of such an extruder.

10 The technique known as reactive extrusion consists in using well-known extrusion devices (more simply called extruders) for the extrusion of materials to be extruded in the melt.

This technique of reactive extrusion is used not only for extruding polymeric materials, in order to synthesize polymeric materials starting from materials to be polymerized, but also for the subsequent chemical conversion of the polymeric materials obtained. These various processes usually require the addition of at least one chemical compound.

A major difficulty encountered when using this technique arises when chemical compounds must be added in the fluidized state. This is because it then becomes very difficult to ensure that they are incorporated into the material to be extruded without problems arising due to the heterogeneous distribution of the chemical compounds in the material to be extruded.

This is all the more so when the amounts of chemical compounds to be introduced are relatively small, for example a few tenths to a few hundreds of microlitres per minute.

25 One of the solutions already proposed in the past is to dilute the chemical compounds in organic solvents. However, major drawbacks are encountered when using these solvents. Among them, mention may especially be made of not only the limited solubility of certain chemical compounds in organic solvents, the toxicity of some of these organic solvents, the time needed to prepare the solutions of chemical compounds in solvents and the removal of the solvent afterwards, but also the occurrence of undesirable side reactions due to the presence of solvent.

Another solution is to impregnate the material to be extruded with the chemical compound or compounds before their introduction into the extruder. However, this solution requires an additional handling step, which is expensive and laborious. In addition, it does not always allow a high degree of flexibility to be achieved as regards introducing chemical compounds.

To remedy the drawbacks of the solutions proposed in the past, the subject of the present invention is firstly a process allowing at least one chemical compound to be incorporated continuously.

For this purpose, the present invention firstly relates to a process for introducing at least one chemical compound into an extruder, in which the following steps are carried out:

- a material to be extruded is introduced into the extruder;
- at least one mixture of at least one chemical compound and of carbon dioxide is introduced into the extruder; and
- the material is extruded together with the mixture or mixtures.

During the latter step of the process according to the invention, the carbon dioxide may or may not be mixed with the material to be extruded as is the chemical compound. Preferably, the carbon dioxide, being in the gaseous state in the extruder, is not mixed with the material to be extruded, and neither is the chemical compound.

The term "extruder" is understood to mean any continuous device comprising at least one feed zone and, at its exit, a discharge zone preceded by a compression zone, the latter forcing the melt to pass through the discharge zone.

The extruder may comprise, in particular, the following parts:

- i. at least one feed zone (feed hopper or injector);
- ii. one or more screw elements used for propagating the material to be extruded;
- iii. optionally, one or more kneading elements;
- iv. one or more heating and/or reaction zones in which the material to be extruded is in the fluiding state; and
- v. at the exit, a compression zone followed by a discharge zone, the compression zone having the function of compressing the material to be extruded so as to force it through the discharge zone of the extruder.

Parts (i) to (v) are not necessarily placed in this order.

Optionally, the discharge zone may furthermore be followed by a granulator or by a device giving the extruded material a profiled shape, such as a film.

Extruders that may be suitable are, in particular, extruders of the single-screw type, extruders of the co-kneader type such as, for example, the extruders sold by Buss, extruders of the interpenetrating or non-interpenetrating corotating twin-screw type as sold by Werner & Pfleiderer, extruders of the interpenetrating or noninterpenetrating, counterrotating twin-screw type and extruders of the multiple-screw type. Advantageously, an extruder based on the work of two screws, whether they are corotating or counterrotating, will be used.

Preferably, in the process for introducing at least one chemical compound into an extruder according to the invention, the mixture or mixtures of at least one chemical compound and of carbon dioxide are introduced into a zone of the extruder where the material to be extruded is in the fluidized state.

Any device allowing the mixture of at least one chemical compound and of carbon dioxide to be introduced can be used. One particularly preferred device is the device according to the invention.

The process according to the invention is also characterized in that the mixture or mixtures of at least one chemical compound and of carbon dioxide are introduced by means of at least one introduction device comprising an injector placed perpendicular to the barrel of the extruder.

Particularly preferably, the mixture or mixtures of at least one chemical compound and of carbon dioxide are introduced by means of an introduction device comprising an injector placed perpendicular to a zone in which the material to be extruded is in the fluidized state.

Depending on the temperature and pressure conditions, the carbon dioxide may be in the liquid, gaseous or supercritical state. If the pressure is above 74 bar and the temperature above 31.4°C, as is usually the case in the extruder used for introducing it into the extruder, the carbon dioxide is in the supercritical state.

The term "chemical compound" is understood to mean, for the purposes of the present invention, any chemical compound chosen from chemical compounds capable of causing a chemical change in a polymeric material, those capable of causing polymerization of a material to be polymerized into a polymeric material (these chemical compounds also being called chemical initiators), but also those which do not cause a chemical change in the polymeric material but which provide them with certain advantages after they have been extruded in the presence thereof. Among this latter category, mention may be made, for example, of conventional additives for polymeric materials (stabilizers, lubricants, etc.).

5 The process according to the invention therefore applies not only to the introduction into the extruder of a single chemical compound as a mixture with carbon dioxide, but also to the introduction of several chemical compounds as a mixture with carbon dioxide and to the introduction of one or more mixtures of one or more chemical compounds as a mixture with carbon dioxide.

The chemical compound or compounds introduced by means of the process according to the invention are preferably in the fluidized state.

10 The expression "chemical in the fluidized state" is understood to mean, for the purposes of the present invention, any chemical compound which is in a fluid state at the temperature and pressure at which it is introduced into the extruder. Among these mention may be made of chemical compounds which are liquid at room temperature, but also chemical compounds which, although being solid at room temperature, are liquid, possibly viscous liquids, at the temperature and pressure of introduction by the device into the extruder.

15 The expression "material to be extruded" is understood to mean, for the purposes of the present invention, any material capable of being extruded. Mention may be made, for example, of polymeric materials, but also materials to be polymerized. The term "a material" is understood to mean, for the purposes of the present invention, both a single material and a mixture of several materials.
20 The process according to the present invention therefore applies not only to one or more polymeric mixtures or one or more materials to be polymerized but also to mixtures of at least one polymeric material and of at least one material to be polymerized.

25 The expression "material to be extruded in the fluidized state" is understood to mean, for the purposes of the present invention, that the material to be extruded, defined above, is in a fluid state, in other words it is a liquid, possibly a viscous liquid, at the temperature and pressure of the extruder. As a general rule, in the process according to the invention, the materials to be polymerized are in the liquid state and the polymeric materials are in the viscous
30 liquid state at the temperature and pressure of the extruder.

The invention also relates to a device for introducing at least one chemical compound into an extruder.

For this purpose, the invention relates to a device for introducing at least one chemical compound into an extruder comprising at least two pumps, a
35 mixing chamber and an injector.

According to an advantageous embodiment, the introduction device

comprises:

- a pump (1) for feeding at least one chemical compound into the mixing chamber;
- a pump (1') for feeding carbon dioxide into the mixing chamber;
- 5 - a mixing chamber; and
- an injector.

The device according to the invention is usually well suited for introducing any chemical compound in the fluidized state.

Thus, the device according to the invention is in general well suited for
10 introducing chemical compounds which are liquid at room temperature. In general, the device according to the invention can also be used to introduce chemical compounds which are solid at room temperature. In the latter case, the device has to be modified so that it can be raised to a temperature such that these chemical compounds are again in a fluidized state, in other words they are
15 liquids, possibly viscous liquids.

The device according to the invention is usually well suited for introducing amounts of chemical compound less than or equal to 2 ml/min., preferably less than or equal to 1 ml/min. and particularly preferably less than or equal to
20 600 μ l/min.

The device according to the invention is usually well suited for introducing amounts of chemical compound greater than or equal to 1 μ l/min., preferably greater than or equal to 3 μ l/min. and particularly preferably greater than or equal to 5 μ l/min.

Preferably, the carbon dioxide is cooled before it enters the pump (1'). To
25 do this, a cryothermostat is generally placed between the carbon dioxide container and the pump (1').

With regard to the pumps used for feeding the chemical compound or compounds and the carbon dioxide into the mixing chamber, any pump allowing small amounts of compounds circulated can be used.

Any mixing chamber ensuring optimum mixing of the chemical compound or compounds introduced in small amount and of the carbon dioxide may be used in the device according to the invention, whether or not it is equipped with a stirring system.

Preferably, the mixing chamber used in the device according to the
35 invention is equipped with a stirring system.

Usually, the amount of chemical compound or compounds in the mixture

of the latter with carbon dioxide in the mixing chamber is less than or equal to 50%, preferably less than or equal to 30% and more particularly less than or equal to 15% by volume.

- Any injector able to work at high pressure may be used in the device
5 according to the invention.

Usually, a pressure sensor is used to measure the pressure in the injector.

The pressure in the injector is usually at least 74 bar, preferably at least 85 bar, particularly preferably at least 90 bar and most particularly preferably at least 100 bar.

- 10 Usually, when the temperature in the injector is high enough, the carbon dioxide is then in the supercritical state in the injector.

Any kind of extruder as defined above may be equipped with the device according to the invention.

- According to another aspect of the present invention, what is also proposed
15 is an extruder which comprises a feed zone, a compression zone and a discharge zone and is equipped with at least one introduction device according to the invention.

- The expression "at least one introduction device" is understood to mean one or more introduction devices which allow one or more chemical compounds
20 to be introduced simultaneously or separately into the stream of material to be extruded.

- The extruder may also contain, preferably after the zone (iv), a venting zone so as to remove the excessive amounts of chemical compounds that have not reacted, carbon dioxide and possibly by-products generated during the
25 extrusion. The carbon dioxide may also be removed via the feed zone of the extruder.

The injector of each introduction device is preferably placed so as to be perpendicular to the barrel of the extruder and emerges tangentially with respect to the extrusion screw flights.

- 30 Advantageously, the injector of each introduction device is placed so as to be perpendicular to a zone where the material to be extruded is in the fluidized state. In this way, the chemical compound or compounds introduced are sprayed onto the material in the fluidized state or injected into the fluidized material.

- Such an extruder is particularly beneficial for the extrusion, chemical
35 modification and synthesis of polymeric materials.

The term "polymeric material" is understood to mean, for the purposes of

the present invention, both a single polymeric material and mixtures of at least two polymeric materials.

Among polymeric materials, mention may be made, for example, of vinyl polymers but also thermoplastic aliphatic polyesters. Among vinyl polymers, mention may be made of homopolymers and copolymers of olefins and halogenated vinyl homopolymers and copolymers. Among the latter, mention may be made of vinylidene fluoride homopolymers and copolymers. Among thermoplastic aliphatic polyesters, mention may be made, for example, of ϵ -caprolactone polymers.

According to another aspect of the present invention, what is also proposed is a process for extruding a polymeric material by means of the extruder described above, in which:

- a polymeric material is introduced into the extruder;
- in each introduction device present:
 - at least one chemical compound is introduced, via a pump, into the mixing chamber,
 - carbon dioxide, precooled, is introduced via a pump into the mixing chamber and
 - the chemical compound or compounds and the carbon dioxide are mixed in the mixing chamber;
- the mixture or mixtures thus obtained are introduced into the extruder; and
- the polymeric material is extruded together with the mixture or mixtures.

According to another aspect of the present invention, what is also proposed is a process for modifying a polymeric material by means of the extruder described above, in which:

- a polymeric material is introduced into the extruder;
- in each introduction device present:
 - at least one chemical compound is introduced via a pump into the mixing chamber,
 - the carbon dioxide, precooled, is introduced via a pump into the mixing chamber and
 - the chemical compound or compounds and the carbon dioxide are mixed in the mixing chamber;
- the mixture or mixtures thus obtained are introduced into the extruder; and
- the polymeric material is extruded together with the mixture or mixtures under conditions allowing a reaction between at least one of the chemical

compounds and the polymeric material.

Such a modification process is particularly beneficial for the modification of polymeric materials, such as those mentioned above, by reaction with a chemical compound such as, for example, an organic peroxide.

According to another aspect of the present invention what is also proposed is a process for synthesizing a polymeric material by means of the extruder described above, in which:

- a material to be polymerized is introduced into the extruder;
- in each introduction device present:
 - at least one chemical compound is introduced via a pump into the mixing chamber,
 - the carbon dioxide, precooled, is introduced via a pump into the mixing chamber and
 - the chemical compound or compounds and the carbon dioxide are mixed in the mixing chamber;
- the mixture or mixtures thus obtained are introduced into the extruder; and
- the material to be polymerized is extruded together with the mixture or mixtures under conditions allowing a reaction between at least one of the chemical compounds and the material to be polymerized, and the polymeric material thus formed is extruded.

In the process for synthesizing a polymeric material according to the invention, at least one of the chemical compounds is a chemical initiator, that is to say a compound capable of initiating the polymerization of the material to be polymerized.

In the process for synthesizing a polymeric material according to the invention, the injector of each device for introducing the chemical initiator or initiators is preferably placed so as to be perpendicular to the feed zone of the extruder.

One advantageous embodiment of the introduction device is described in greater detail by way of illustration in Figure 1.

Figure 1 shows a container 6 for a chemical compound (there could be several of them within the meaning of the present invention) which is fed into the mixing chamber 2 by means of a pump 1. The carbon dioxide contained in the container 4 is cooled in the cryothermostat 3 before being fed into the mixing chamber 2 by means of a pump 1'. The mixture of the chemical compound or compounds (if there are several containers) and of the carbon dioxide which is

produced in the mixing chamber is then discharged into the injector 7, the pressure of which is measured by means of a pressure sensor 5.

The device according to the invention has many advantages. Thus, it allows one or more chemical compounds to be continuously incorporated into a material to be extruded. Moreover, it allows small amounts of this or these chemical compound or compounds to be introduced, with a uniform rate of introduction which may moreover be kept constant, even when the flow rates of chemical compounds are particularly low. The device according to the invention furthermore avoids the use of organic solvents, the disadvantages of which were mentioned above. It also avoids relatively long purging times and extensive and difficult cleaning of the plant. Finally, the device according to the invention has the advantage of a higher degree of flexibility with regard to the amount of the chemical compound or compounds to be introduced and with regard to the point at which the introduction of the chemical compound or compounds can take place.

The example which follows serves to illustrate the present invention without thereby limiting the scope thereof.

Example

This example describes the modification of an ϵ -caprolactone polymer by the reaction of the latter with a chemical compound which is an organic peroxide.

ϵ -Caprolactone polymer

The ϵ -caprolactone polymer was poly- ϵ -caprolactone CAPA[®]680 sold by Solvay Interox.

It was characterized by a number-average molecular mass of 70 000 g/mol. The molecular mass was measured by gel permeation chromatography using chloroform as solvent, by means of a column of the Polymer Laboratories Mix-C type and a refractometer of the Waters Differential Refractometer R401 type. The concentration of the specimen was 20 mg/ml and the flow rate was 1 ml/min. The standards used were polystyrene standards and the conversion factor used was 0.6.

The poly- ϵ -caprolactone was characterized by a melting point of 58-60°C, measured by differential thermal analysis, in the second pass and with a scan rate of 10 K/min.

The poly- ϵ -caprolactone was also characterized by an MFI of 2.11 dg/min., obtained by measuring the amount of polymer passing through a calibrated

cylindrical die (height: $8 \text{ mm} \pm 0.025 \text{ mm}$; diameter: $2.095 \text{ mm} \pm 0.003 \text{ mm}$) at a temperature of 100°C and under a load of 5 kg.

Organic peroxide

- 5 The organic peroxide was 2,5-dimethyl-2-5-di-*tert*-butylperoxyhexane (DHBP) sold under the brand name LUPERSOL®101 by Peroxid Chemie.

Extruder

- The extruder used was a Werner & Pfleiderer ZSK®40 corotating double-screw extruder. The diameter of the screws was 40 mm and their length was 1 360 mm. The rotation speed of the screws was 200 rpm (rotations per minute).
- 10 The extruder was designed so that it comprised, in succession, a feed zone, a material melting zone, a homogenization zone, a reaction zone and a discharge zone preceded by a compression zone. Each of these zones was at a very specific temperature.

The feed zone was at a temperature less than or equal to 20°C .

- 15 The material melting zone was at a temperature of 130°C , the DHBP was introduced into this mixing zone with the carbon dioxide by means of the introduction device described above.

The homogenization zone was at a temperature of 130°C .

The reaction zone was at a temperature of 180°C .

- 20 The compression zone was at a temperature of 180°C .

The discharge zone was at a temperature of 180°C .

Introduction device

- The device for introducing the mixture of the organic peroxide and carbon dioxide is shown schematically in Figure 1.

- 25 The DHBP contained in the container 6 was fed into the mixing chamber 2 by means of the pump 1. The liquid carbon dioxide contained in the container 4 was cooled to -10°C in the cryothermostat 3 before being fed into the mixing chamber 2 by means of a pump 1'. The mixture of DHBP and liquid carbon dioxide produced in the mixing chamber was then discharged into the injector 7, the pressure of which was measured by means of a pressure sensor 5.
- 30

The liquid carbon dioxide container 4 was a pressurized carbon dioxide cylinder.

- The pumps 1 and 1' were pumps of the Gilson 305 or 306 type. The head of the pump 1' designed for carbon dioxide was fitted with a Gilson 5/10/25SG kit allowing the head to be cooled to -10°C . The coolant was isopropanol cooled in a JUBALO F30-type cryothermostat.
- 35

The same cryothermostat was used to cool the liquid carbon dioxide (cryothermostat 3).

The mixing chamber 2 was an analytical mixer provided with a Gilson 811C-type stirrer.

- 5 The injector 7 was an injector for working at high pressure (above 74 bar).

A pressure sensor 5 of the Gilson 806 type was placed between the pump 1' and the mixing chamber 2 so as to measure the pressure (between 90 and 120 bar) in the injector.

- 10 The injector of the introduction device was placed so as to be perpendicular to the barrel of the extruder and emerged tangentially with respect to the extrusion screw flights. It was placed specifically so as to be perpendicular to the melting zone of the extruder. The carbon dioxide was generally in the supercritical state within the injector.

Modification of the ϵ -caprolactone polymer by DHBP

- 15 The poly- ϵ -caprolactone CAPA®680 was introduced into the feed zone of the extruder described above at a rate of 30 kg/h and propagated along the various zones of the extruder.

- 20 In the melting zone of the extruder, the DHBP, as a mixture with carbon dioxide, was sprayed onto the poly- ϵ -caprolactone by means of the introduction device described above. The DHBP was introduced in an amount of 1 g per kg of poly- ϵ -caprolactone CAPA®680 and in an amount of 570 μ l of DHBP in 5 ml of carbon dioxide per minute.

- 25 The poly- ϵ -caprolactone obtained was characterized by an MFI of 0.42 dg/min., obtained by measuring the amount of polymer passing through a calibrated cylindrical die (height: 8 mm \pm 0.025 mm; diameter: 2.095 mm \pm 0.003 mm) at a temperature of 100°C and under a load of 5 kg.

CLAIMS

1. Process for introducing at least one chemical compound into an extruder, characterized in that the following steps are carried out :

- a material to be extruded is introduced into the extruder;
- 5 - at least one mixture of at least one chemical compound and of carbon dioxide is introduced into the extruder by means of at least one introduction device comprising at least two pumps, a mixing chamber and an injector which is placed so as to be perpendicular to the barrel of the extruder; and
- the material is extruded together with the mixture or mixtures.

- 10 2. Process according to Claim 1, characterized in that the mixture or mixtures of at least one chemical compound and of carbon dioxide are introduced into a zone of the extruder where the material to be extruded is in the fluidized state.

- 15 3. Process according to either of Claims 1 and 2, characterized in that the chemical compound or compounds are in the fluidized state.

4. Device for introducing at least one chemical compound into an extruder, characterized in that it comprises at least two pumps, a mixing chamber and an injector.

- 20 5. Device according to Claim 4, characterized in that it comprises:
- a pump (1) for feeding at least one chemical compound into the mixing chamber;
 - a pump (1') for feeding carbon dioxide into the mixing chamber;
 - a mixing chamber; and
 - an injector.

- 25 6. Device according to Claim 5, characterized in that the carbon dioxide is cooled before it enters the pump (1').

7. Device according to any one of Claims 4 to 6, characterized in that the mixing chamber is equipped with a stirring system.

- 30 8. Device according to any one of Claims 4 to 7, characterized in that the pressure in the injector is measured by means of a pressure sensor.

9. Extruder, comprising a feed zone, a compression zone and a discharge zone, equipped with at least one introduction device according to one of Claims 4 to 8.

10. Extruder according to Claim 9, comprising an extrusion screw and a barrel, in which the injector of each introduction device is placed so as to be perpendicular to the barrel of the extruder and emerges tangentially with respect to the extrusion screw flights.

11. Extruder according to either of Claims 9 and 10, in which the injector of each introduction device is placed so as to be perpendicular to a zone in which the material to be extruded is in the fluidized state.

12. Process for extruding a polymeric material by means of an extruder according to any one of Claims 9 to 11, characterized in that:

- a polymeric material is introduced into the extruder;
- in each introduction device present:
 - 15 - at least one chemical compound is introduced, via a pump, into the mixing chamber,
 - carbon dioxide, precooled, is introduced via a pump into the mixing chamber and
 - 20 - the chemical compound or compounds and the carbon dioxide are mixed in the mixing chamber;
- the mixture or mixtures thus obtained are introduced into the extruder; and
- the polymeric material is extruded together with the mixture or mixtures.

13. Process for modifying a polymeric material by means of an extruder according to any one of Claims 9 to 11, characterized in that:

- 25 - a polymeric material is introduced into the extruder;
- in each introduction device present:
 - at least one chemical compound is introduced via a pump into the mixing chamber,
 - 30 - the carbon dioxide, precooled, is introduced via a pump into the mixing chamber and
 - the chemical compound or compounds and the carbon dioxide are mixed in the mixing chamber;
- the mixture or mixtures thus obtained are introduced into the extruder; and
- the polymeric material is extruded together with the mixture or mixtures under

conditions allowing a reaction between at least one of the chemical compounds and the polymeric material.

14. Process for synthesizing a polymeric material by means of an extruder according to any one of Claims 9 to 11, characterized in that:

- 5 - a material to be polymerized is introduced into the extruder;
- in each introduction device present:
 - at least one chemical compound is introduced via a pump into the mixing chamber,
 - 10 - the carbon dioxide, precooled, is introduced via a pump into the mixing chamber and
 - the chemical compound or compounds and the carbon dioxide are mixed in the mixing chamber;
- the mixture or mixtures thus obtained are introduced into the extruder; and
- 15 - the material to be polymerized is extruded together with the mixture or mixtures under conditions allowing a reaction between at least one of the chemical compounds and the material to be polymerized, and the polymeric material thus formed is extruded.

ABSTRACT

Process for introducing at least one chemical compound into an extruder, introduction device, extruder equipped with such a device and processes using such an extruder

Process for introducing at least one chemical compound into an extruder, in which the following steps are carried out:

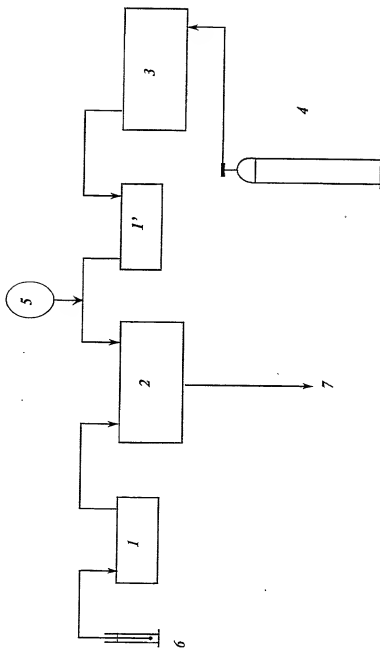
- a material to be extruded is introduced into the extruder;
- at least one mixture of at least one chemical compound and of carbon dioxide is introduced into the extruder; and
- the material is extruded together with the mixture or mixtures.

Device for introducing at least one chemical compound into an extruder. Extruder equipped with at least one introduction device. Process for extruding, process for modifying and process for synthesizing a polymeric material by means of such an extruder.

Single figure.

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200540-4410001

#4

Declaration and Power of Attorney for Patent Application

Déclaration et Pouvoirs pour Demande de Brevet

French Language Declaration

En tant l'inventeur nommé ci-après, je déclare par le présent acte que:

As a below named inventor, I hereby declare that:

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom.

My residence, post office address and citizenship are as stated next to my name.

Je crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de brevet a été déposée concernant l'invention intitulée

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Process for introducing at least one chemical compound into an extruder, introduction device, extruder equipped with such a device and processes using such an extruder"

et dont la description est fournie ci-joint à moins

the specification of which:

☐ ci-joint

☐ is attached hereto.

☒ a été déposée le 20/07/2000

☐ was filed on _____

sous le numéro de demande des États-Unis ou le numéro de demande international PCT

as United States Application Number or PCT International Application Number

PCT/EP00/06970 et modifiée le

_____ and was amended on

_____ (le cas échéant).

_____ (if applicable).

Je déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, telles qu' modifiées par toute modification dont il aura été fait référence ci-dessus.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

Je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

French Language Declaration

Je revendique par le présent acte avoir la priorité étrangère, en vertu du Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et figurant ci-dessous et, en cochant la case, j'ai aussi indiqué ci-dessous toute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiquée.

Prior Foreign Application(s)
Demande(s) de brevet antérieure(s) dans un autre pays.

09900511 Belgium
(Number) (Country)
(Numéro) (Pays)

(Number) (Country)
(Numéro) (Pays)

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority claimed
Droit de priorité
revendiqué

27/07/1999
(Day/Month/Year Filed)
(Jour/Mois/Anné de dépôt)

☒ ☐
Yes No
Oui Non

(Day/Month/Year Filed)
(Jour/Mois/Anné de dépôt)

☐ ☐
Yes No
Oui Non

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 119(e) du Code des Etats-Unis, de toute demande de brevet provisoire effectuée aux Etats-Unis et figurant ci-dessous.

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

(Application No.) (Filing Date)
(N° de demande) (Date de dépôt)

(Application No.) (Filing Date)
(N° de demande) (Date de dépôt)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 120 du Code des Etats-Unis, de toute demande de brevet effectuée aux Etats-Unis, ou en vertu du Titre 35, § 365(c) du même Code, de toute demande internationale PCT désignant les Etats-Unis et figurant ci-dessous et, dans la mesure où l'objet de chacune des revendications de cette demande de brevet n'est pas divulgué dans la demande antérieure américaine ou internationale PCT, en vertu des dispositions du premier paragraphe du Titre 35, § 112 du Code des Etats-Unis, je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations, dont j'ai pu disposer entre la date de dépôt de la demande antérieure et la date de dépôt de la demande nationale ou internationale PCT de la présente demande.

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

PCT/EP00/06970 20/07/2000
(Application No.) (Filing Date)
(N° de demande) (Date de dépôt)

patented
(Status) (patented, pending, abandoned)
(Statut) (breveté, en cours d'examen, abandonné)

(Application No.) (Filing Date)
(N° de demande) (Date de dépôt)

(Status) (patented, pending, abandoned)
(Statut) (breveté, en cours d'examen, abandonné)

Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, véridique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour véridique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d'une incarceration, ou des deux, en vertu de la Section 1001 du Titre 18 du Code des Etats-Unis, et que de telles déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celle-ci.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

French Language Declaration

POUVOIRS: En tant que l'inventeur cité, je désigne par la présente l'(les) avocat(s) et/ou agent(s) suivant(s) pour qu'il(s) poursuive(nt) la procédure de cette demande de brevet et traite(nt) toute affaire s'y rapportant avec l'Office des brevets et des marques: (mentionner le nom et le numéro d'enregistrement).

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)

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Signature du co-inventeur <i>Gauthy F.</i>	Date <i>04.02.2002</i>	Second inventor's signature	Date
Domicile: Ch. P. De Waet, 38 B-1780 WEMMEL (Belgium)		Residence	
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(Fournir les mêmes renseignements et la signature de tout co-inventeur supplémentaire.)

(Supply similar information and signature for third and subsequent joint inventors.)